

Radiative charge transfer in cold and ultracold Sulfur atoms colliding with Protons

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Abstract. Radiative decay processes at cold and ultra cold temperatures for Sulfur atoms colliding with protons are investigated. The MOLPRO quantum chemistry suite of codes was used to obtain accurate potential energies and transition dipole moments, as a function of internuclear distance, between low-lying states of the SH^+ molecular cation. A multi-reference configuration-interaction (MRCI) approximation together with the Davidson correction is used to determine the potential energy curves and transition dipole moments, between the states of interest, where the molecular orbitals (MO's) are obtained from state-averaged multi-configuration-self-consistent field (MCSCF) calculations. The collision problem is solved approximately using an optical potential method to obtain radiative loss, and a fully two-channel quantum approach for radiative charge transfer. Cross sections and rate coefficients are determined for the first time for temperatures ranging from $10 \mu\text{K}$ up to $10,000\text{ K}$. Results are obtained for all isotopes of Sulfur, colliding with H^+ and D^+ ions and comparison is made to a number of other collision systems.

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1. Introduction

Molecule formation processes involving second-row elements are of considerable interest as searches are ongoing in a variety of interstellar and circumstellar media [1, 2]. The SH^+ cation has been observed in absorption recently in the diffuse interstellar medium [3]. The growth of state selective ultracold quantum chemistry is another motivation for this work [4]. Here we have investigated radiative decay processes at ultracold temperatures and above for Sulfur atoms colliding with protons.

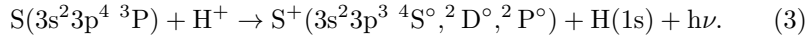
Radiative association is the direct combination of two particles, neutral or ionized, with de-excitation of the formed molecule by emission of a photon. For this process to be efficient it is necessary that the molecule be formed in a state linked, by permitted transitions, to the fundamental level, so that it can get rid of its excess energy by emission of a photon. Previously Stancil et al. [1], studied this system for radiative association in the ground electronic state for S^+ ions colliding with atomic hydrogen,



while Zhao et al. [5] performed close-coupling calculations of the direct or non-radiative, charge transfer process,



In this work, we use accurate potential energies and transition dipole moments as input to perform collision cross section calculations for the radiative charge transfer process of Sulfur atoms colliding with protons. The present collision problem is solved using an optical potential method and a fully quantal approach in order to obtain the radiative charge transfer cross sections for the process [6],



For excited states of this cation, for the first time rate coefficients for reaction (3) are determined by averaging over a Maxwellian velocity distribution.

Rate coefficients are of interest for theoretical models of photodissociation regions (PDRs) and X-ray-dominated regions (XDRs) as S^+ ion-chemistry may be important [7]. S^+ ion-chemistry may also play a role in the X-ray chemistry in the envelopes around young stellar objects [2]. For the similar ion CH^+ the rate coefficient for its formation via radiative association ranges between 10^{-14} and $10^{-13}\text{cm}^3\text{s}^{-1}$. The formation rates for SH^+ are expected to be comparable. Here we determine rate coefficients for temperatures ranging from $10\ \mu\text{K}$ up to $10,000\text{K}$ for these applications and also investigate isotope effects. Our results are compared to a number of other ion-atom collision systems.

The layout of this paper is as follows. In section 2 we give a brief outline of the theoretical approaches used to determine the cross sections and rate coefficients. Section 3 presents the results from our work and finally in section 4 conclusions are drawn from our present investigations. Atomic units are used throughout unless otherwise noted.

2. Theory

2.1. Electronic structure calculations

Following our earlier work on this molecular cation [1] for radiative association, we extend our computations using a parallel version of the MOLPRO [8] suite of *ab*

initio quantum chemistry codes (release MOLPRO 2010.1) to calculate the molecular structure of this diatomic hydride SH^+ to higher-lying triplet electronic states and the transition dipole matrix elements connecting the states. Potential energy curves and transition dipole moments as a function of internuclear distance are computed out to a bond separation of $R = 18$ a.u. For separations beyond this, we use a multipole expansion to represent the long-range part of the potentials. We conducted Multi-Reference Configuration Interaction (MRCI) calculations on the State-Averaged Multi-Configuration-Self-Consistent-Field (SA-MCSCF) wavefunctions [9]. The Davidson correction was applied to all our results [10]. This multi-reference configuration interaction (MRCI) approach with the Davidson correction was used to calculate all the potentials for this molecular cation as it dissociates. To model the all-electron calculations, we use an augmented-correlation-consistent polarized valence sextuplet Gaussian basis set; aug-cc-pV6Z (AV6Z). The choice of this AV6Z basis is due to the fact that in quantum chemistry calculations these large Gaussian basis sets are well known to recover ~ 99 % of the electron correlation energy [9]. All our electronic structure computations were performed in the C_{2v} Abelian point group symmetry (A_1, B_1, B_2, A_2). In the C_{2v} point group, all molecular orbitals were labeled by their symmetry (a_1, b_1, b_2, a_2); when symmetry is reduced from $C_{\infty v}$ to C_{2v} , the correlating relationships are $\sigma \rightarrow a_1$, $\pi \rightarrow (b_1, b_2)$, $\delta \rightarrow (a_1, a_2)$. The active space consists of 16 electrons and 10 molecular orbitals $6a_1, 2b_1, 2b_2, 0a_2$ (6 2 2 0). To take account of short-range interactions we employed the multi-configuration-self-consistent-field (MCSCF) method [11, 12] available within the MOLPRO [8] suite of codes. The molecular orbitals for the MRCI method were obtained from the state-averaged-multi-configuration-self-consistent-field method (SA-MCSF). The averaging processes was carried out on the lowest four $^3\Pi$, three $^3\Sigma^-$ and three $^3\Delta$ molecular states of this cation.

In Fig. 1 we illustrate all the triplet states involved in the radiative decay processes. All the potential energies in Fig. 1 are given in eV relative to the ground-state equilibrium bond distance r_e of this cation. Note, radiative charge transfer can occur either from the $3\ ^3\Sigma^-$ or the $3\ ^3\Pi$ state (the entrance channels). The $3\ ^3\Sigma^-$ has a shallow well whereas the $3\ ^3\Pi$ state is totally repulsive. Table 1 gives asymptotic properties of the molecular states.

Figs. 2 illustrates the dipole transition moments $D(R)$ as a function of internuclear separation R connecting the $3\ ^3\Sigma^-$ to the lower lying triplet electronic states involved in the dynamics. In Fig. 3 the corresponding transition dipole moments connecting the $3\ ^3\Pi$ entrance channel are shown. The results in Figs. 2 and 3 are obtained from the MRCI+Q calculations using an AV6Z basis. We note that the asymptotic separated-atom energies in the MRCI+Q approximation show suitable agreement with experimental atomic values (see Table 1).

Our results show smooth dipole moments connecting all of the adiabatic triplet states which leads us to conclude that the sensitivity of the radiative transitions will be primarily due to the nuclei wave function envelope. The resonance behaviour will be primarily due to potential scattering in the elastic scattering channel.

The spontaneous decay rate $\Gamma(R)$ (see below) decreases exponentially as R increases due to the exponential attenuation in the overlap of the atomic wave functions corresponding to charge transfer. Beyond $R = 18$ a.u., the potential of the $3\ ^3\Sigma^-$ or $3\ ^3\Pi$ excited state (the entrance channel, see Fig. 1) can be approximated

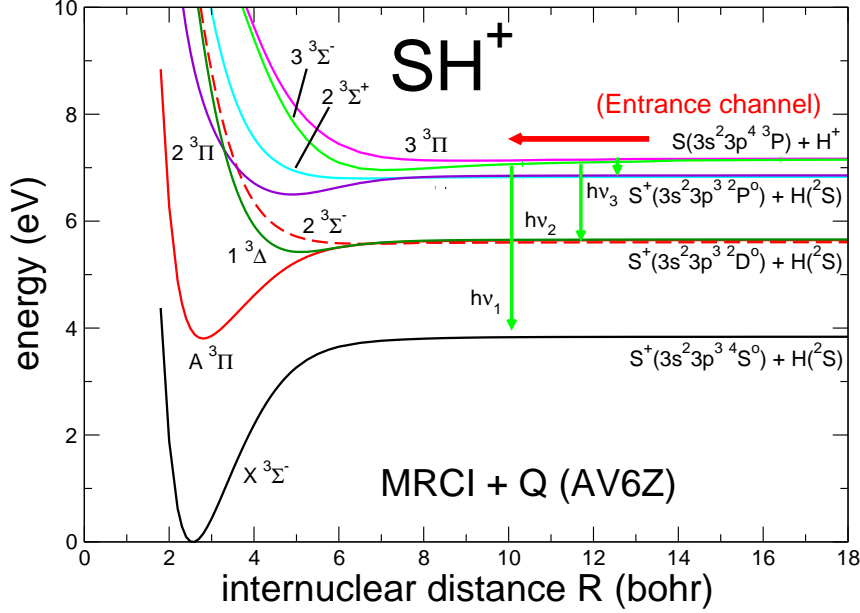


Figure 1. (Colour online) Relative electronic energies (eV) for the SH^+ molecular cation as a function of bond separation at the MRCI+Q level of approximation with an AV6Z basis. The $3^3\Sigma^-$ and $3^3\Pi$ entrance channels of the $S(3s^2 3p^4 ^3P) + H^+$ cation are shown together with lower lying triplet electronic states ($3^3\Sigma^-$, $3^3\Sigma^+$, $3^3\Pi$ and $3^3\Delta$) for which radiative charge transfer may occur. The allowed radiative transitions from the entrance channels equation (3) are indicated by the vertical lines.

by the long-range multipole expansion:

$$V(R) = \frac{Q_M}{2R^3} - \frac{\alpha_d}{2R^4} + V(+\infty), \quad (4)$$

where Q_M is the quadrupole moment and α_d is the dipole polarizability of the neutral atom. Q_M for a p^4 configuration is $-\frac{4}{5}e < r^2 >$ for a Σ state and $\frac{2}{5}e < r^2 >$ for a Π state [13], where the $< r^2 >$ value for Sulfur is 5.065255 a.u (3P state) [14, 15] and $Q_M = 0$ for H. The atomic values for the dipole polarizability adopted here are respectively, $\alpha(S)=18.0$ and $\alpha(H)=4.5$. The long-range expansion of the final channel has just the last 2 terms of the right hand side in (4). At short range internuclear distances we fitted the potentials with the form,

$$V = Ae^{-BR} + C \quad (5)$$

where A , B and C are fitting constants. A similar approach was used for the transition dipole moments to extend to long and short range internuclear distances for our cross section calculations.

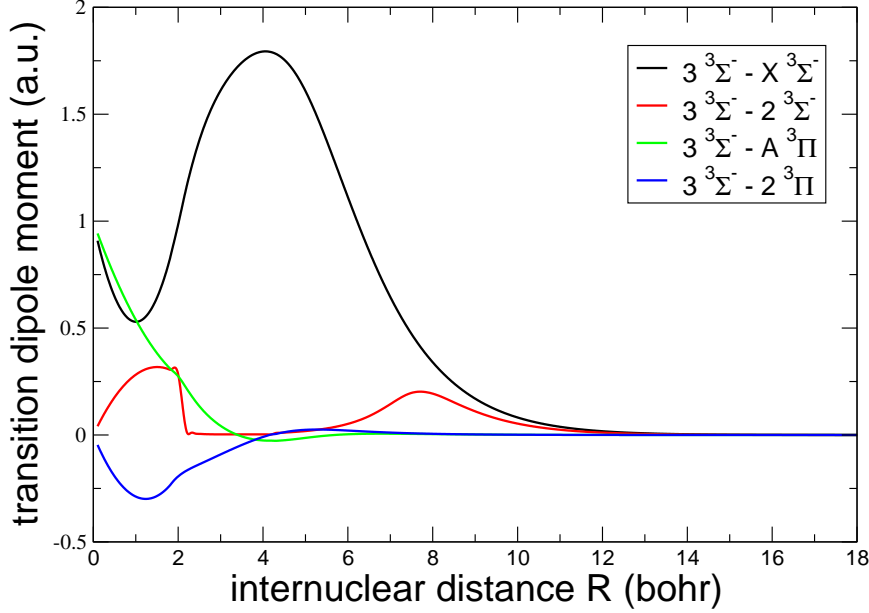


Figure 2. (Colour online) Dipole transition moments $D(R)$ for the $3^3\Sigma^- \rightarrow X^3\Sigma^-, 2^3\Sigma^-, 2^3\Pi, A^3\Pi$ transitions. The MRCI + Q approximation with an AV6Z basis set is used to calculate the transition dipole moments.

2.2. Dynamics

In the simple classical scattering model [18], the nuclear motion takes place on the ion-atom incoming potential surface, $V(R)$. Thus in a first approximation the motion is angular-momentum conserving, time-reversal invariant, and elastic. With the centre-of-mass frame denoted as E and the reduced mass of the nuclei as μ , then we take, $V(+\infty) = 0$. So for an impact parameter, b , the semi-classical cross-section is simply,

$$\sigma_c(E) = 2\pi \int_0^{+\infty} bP(E, b)db, \quad (6)$$

where $P(E, b)$ is the capture probability.

Since the radial velocity can be written as,

$$v_R^2(R) = \frac{2E}{\mu} \left(1 - \frac{V(R)}{E} - \frac{b^2}{R^2} \right), \quad (7)$$

then the classical turning point will be the (largest) solution of the equation:

$$\frac{dR(t)}{dt} = v_R(R_c) = 0. \quad (8)$$

The process of spontaneous emission has a rate $\Gamma(R)$ which drives the charge transfer process. One can write for the probability of emission, for example as explained in

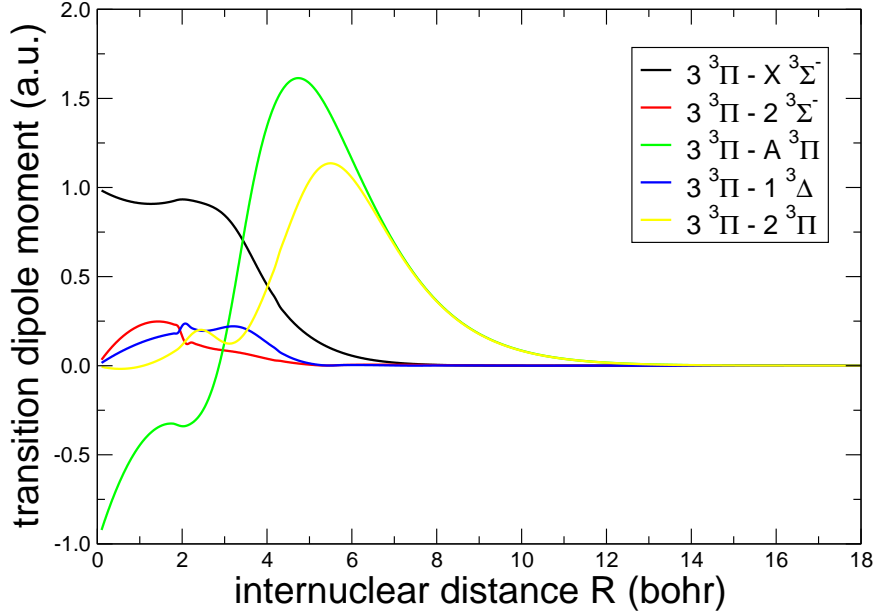


Figure 3. (Colour online) Dipole transition moments $D(R)$ (in atomic units) for the $3^3\Pi \rightarrow X^3\Sigma^-, 2^3\Sigma^-, A^3\Pi, 1^3\Delta, 2^3\Pi$ transitions. The MRCI+Q approximations with an AV6Z basis set is used to calculate the transition dipole moments.

[18], for weak coupling as:

$$P(b, E) \approx 2 \int_{R_c}^{+\infty} \frac{\Gamma(R)}{v_R(R)} dR, \quad (9)$$

which leads directly to the expression,

$$\sigma_c(E) = 2\pi \sqrt{\frac{2\mu}{E}} \int_0^{+\infty} b db \int_{R_c}^{\infty} \frac{\Gamma(R) dR}{\sqrt{1 - V(R)/E - b^2/R^2}}. \quad (10)$$

At high energies, $E \gg V$, the trajectory is almost rectilinear and the integrand is energy independent and thus $\sigma(E) \sim (\mu/E)^{1/2}$. It is purely by coincidence that this energy dependence, which arises from the collision time, matches the classical Langevin model [19] for reactive collisions. The optical potential method, in the context of radiative charge transfer, has been described in detail by Dalgarno and co-workers [22, 23, 24]. In the adiabatic approximation the dynamics occur on decoupled, centrally-symmetric potential energy curves. In the ultracold regime ($E < 1$ meV) all non-adiabatic radial and rotational coupling are weak and the vacuum coupling (by photo-emission) is the dominant non-elastic process. The ion-atom collision channel thus becomes a resonance state, with an effective potential associated

Table 1. Asymptotic Separated-atom and United-atom limit Properties of the molecular states included in our present work.

Molecular State	Separated-atom		United-atom Cl^+		
	Atomic states	Energy (eV)		State	Dipole Moment ^c (a.u.)
		Theory ^a	Expt. ^b		
$3\ ^3\Sigma^-$	$S(3s^23p^4\ ^3P) + H^+(^1S_g)$	0.00	0.00	$3s^23p^3(^4S^o)3d\ ^3D^o$	-
$2\ ^3\Pi$	$S^+(3s^23p^3\ ^2P^o) + H(^2S_{\frac{1}{2}})$	-0.31	-0.22	$3s3p^5\ ^3P^o$	0.0
$A\ ^3\Pi$	$S^+(3s^23p^3\ ^2D^o) + H(^2S_{\frac{1}{2}})$	-1.52	-1.42	$3s^23p^4\ ^3P$	0.997
$2\ ^3\Sigma^-$	$S^+(3s^23p^3\ ^2D^o) + H(^2S_{\frac{1}{2}})$	-1.51	-1.42	$3s^23p^3(^4S^o)4s\ ^3S^o$	0.0
$X\ ^3\Sigma^-$	$S^+(3s^23p^3\ ^4S^o) + H(^2S_{\frac{1}{2}})$	-3.32	-3.26	$3s^23p^4\ ^3P$	0.997
$3\ ^3\Pi$	$S(3s^23p^4\ ^3P) + H^+(^1S_g)$	-0.00	0.00	$3s^23p^3(^4S^o)3d\ ^3D^o$	-
$2\ ^3\Pi$	$S^+(3s^23p^3\ ^2P^o) + H(^2S_{\frac{1}{2}})$	-0.31	-0.22	$3s3p^5\ ^3P^o$	0.0
$1\ ^3\Delta$	$S^+(3s^23p^3\ ^2D^o) + H(^2S_{\frac{1}{2}})$	-1.51	-1.42	$3s^23p^3(^4S^o)3d\ ^3D^o$	0.0
$A\ ^3\Pi$	$S^+(3s^23p^3\ ^2D^o) + H(^2S_{\frac{1}{2}})$	-1.52	-1.42	$3s^23p^4\ ^3P$	-0.997
$2\ ^3\Sigma^-$	$S^+(3s^23p^3\ ^2D^o) + H(^2S_{\frac{1}{2}})$	-1.51	-1.42	$3s^23p^3(^4S^o)4s\ ^3S^o$	0.0
$X\ ^3\Sigma^-$	$S^+(3s^23p^3\ ^4S^o) + H(^2S_{\frac{1}{2}})$	-3.33	-3.26	$3s^23p^4\ ^3P$	0.997

^aMRCI+Q (AV6Z basis).^bDeduced from NIST Atomic Spectra Database tabulations [16].^cTransition dipole moments with initial states, deduced from [17].

with the radiative shift and width. The physics is thus reduced to an optical potential: single channel (complex central potential) scattering problem:

$$V_c(R) = V(R) - \frac{1}{2}i\ \Gamma(R), \quad (11)$$

where $V(R)$ is the real (shifted) adiabatic potential in the ion-atom collision potential.

In this paper, the imaginary part of optical potential method represents loss though radiative emission, which include decay to a bound or continuum state of the molecule ion. That is, implicitly, and approximately, we include both the process of radiative association and radiative charge transfer. This point is discussed in detail in recent applications [25, 26] and its validity verified. In other terms, the Einstein spontaneous decay rate Γ , which is larger the higher the photon frequency, is taken as a vertical transition in analogy to the way that the ‘reflection principle’ is applied [27]. This approximation becomes more accurate the heavier the mass of the colliding atoms/ions, since the momentum (local wavelength) of the nuclei is conserved when the reduced mass is larger. The problem can be summarized mathematically [25] as the solution of the Schrödinger equation,

$$\left[-\frac{1}{2\mu} \nabla_{\mathbf{R}}^2 + V(R) - E \right] F(E; \mathbf{R}) = \frac{1}{2}i\ \Gamma(R)F(E; \mathbf{R}), \quad (12)$$

where,

$$\Gamma(R) = \frac{4D^2(R)}{3c^3} |V(R) - V_f(R)|^3, \quad (13)$$

and, using atomic units, c is the speed of light, where $V(R)$ and $V_f(R)$ are the adiabatic potentials of the upper (initial) and lower (final) electronic state. Since the overlap of the electronic states involved in the charge transfer is large only at short-range, $\Gamma(R)$ is exponentially damped with increasing R . As the potential is central, even though

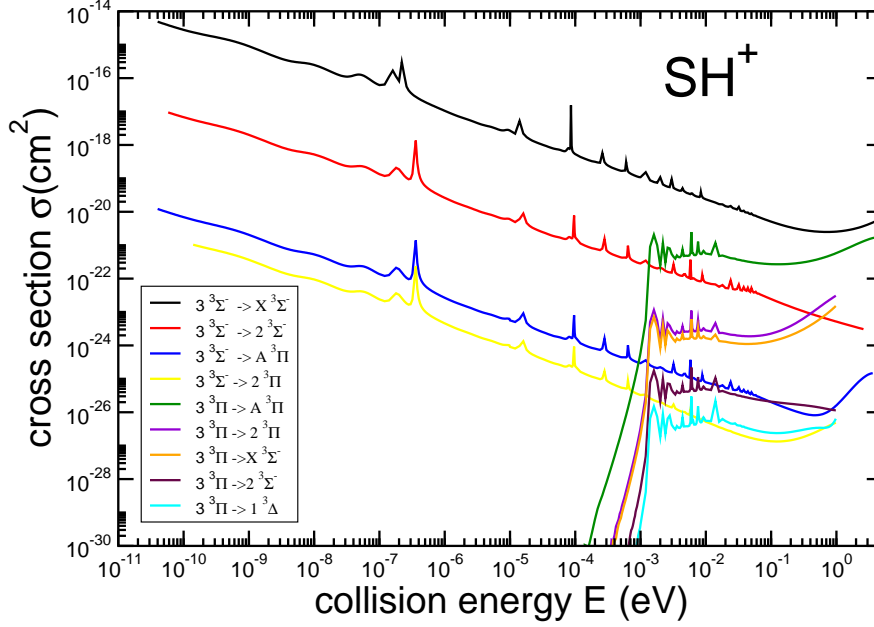


Figure 4. (Colour online) Cross section σ (cm^2) for radiative charge transfer as a function of centre of mass collision energy E (eV), for the nine allowed transitions obtained with the optical potential method, see text for details. In the figure we present the spinless cross sections, that is $g = 1$.

it is complex, the usual separation in spherical coordinates applies, and the scattering wavefunction can be decomposed as,

$$F(E; \mathbf{R}) = \sum_{J, M_J} \chi_J(k, R) Y_{JM_J}(\hat{\mathbf{R}}), \quad (14)$$

where Y_{JM_J} and χ_J are the spherical harmonics and radial wave function, respectively. We define the elastic-scattering wavenumber, $k_J(R)$, for the initial ion-atom channel with angular momentum J , as follows:

$$k_J^2(R) = k^2 - 2\mu V(R) - J(J+1)/R^2. \quad (15)$$

The collision wavenumber is defined as

$$k = \lim_{R \rightarrow \infty} k_J \quad (16)$$

and the corresponding radial functions, $f_{u,J}(k, R) = kR\chi_{u,J}(k, R)$, will be the solutions of the equations:

$$\left[\frac{d^2}{dR^2} + k_J^2(R) \right] f_J(k, R) = 0. \quad (17)$$

This is normalized asymptotically ($R \rightarrow \infty$) according to,

$$f_J(k, R) \rightarrow \sqrt{\frac{2\mu}{\pi k}} \sin \left(kR - \frac{1}{2}J\pi + \delta_J \right) \quad (18)$$

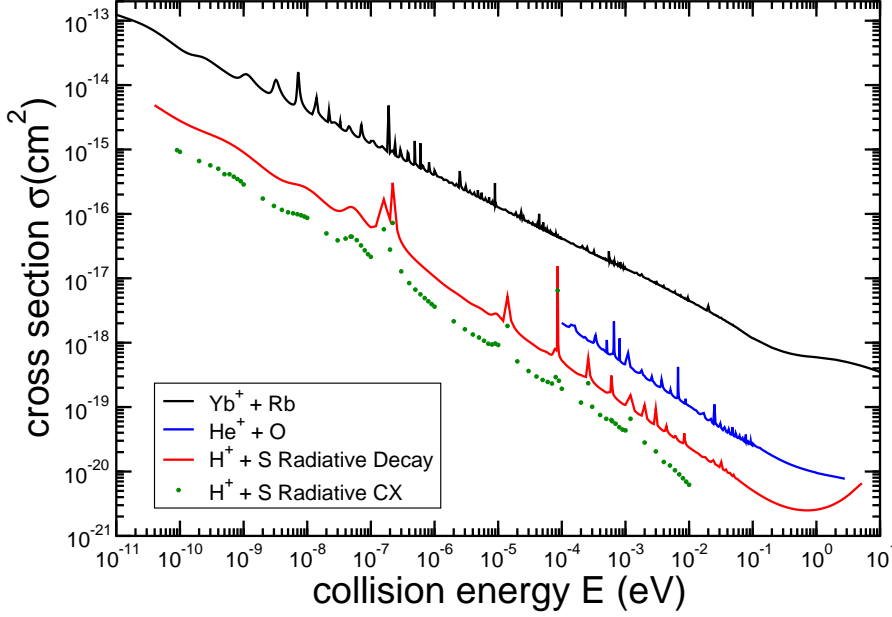


Figure 5. (Colour online) Total radiative charge transfer cross sections for $H^+ + S$, $He^+ + O$ [20] and $Yb^+ + Rb$ [21]. Cross sections σ are in (cm^2) as a function of centre of mass collision energy E (eV), for the various systems, see text for details.

and δ_J is the elastic phase shift. When the optical potential is used the radial equations for the functions in (14) are the same:

$$\left[\frac{d^2}{dR^2} + \kappa_J^2(R) \right] f_{cJ}(k, R) = 0, \quad (19)$$

apart from the modification for the complex wavenumber:

$$\kappa_J^2(R) = k_J^2(R) - i\mu\Gamma(R), \quad (20)$$

and the corresponding complex radial function, f_{cJ} .

The imaginary term is short-ranged, so the asymptotic wavenumber, and hence the normalisation conventions (and density of states) for the radial wavefunctions (18) are the same. However, the partial waves, $f_{cJ}(k, R)$, have complex phase shifts [28] and thus the outgoing probability flux is attenuated.

Naturally the vacuum emission represented by the width $\Gamma(R)$ is much smaller in magnitude compared with the real potential $V(R)$ and thus we can solve (19) by perturbation theory. In the distorted-wave approximation the imaginary part of the phase shift, μ_J^{DW} , is given by

$$\mu_J^{DW}(k) = \frac{\pi}{2} \int_0^{+\infty} |f_J(k, R)|^2 \Gamma(R) dR. \quad (21)$$

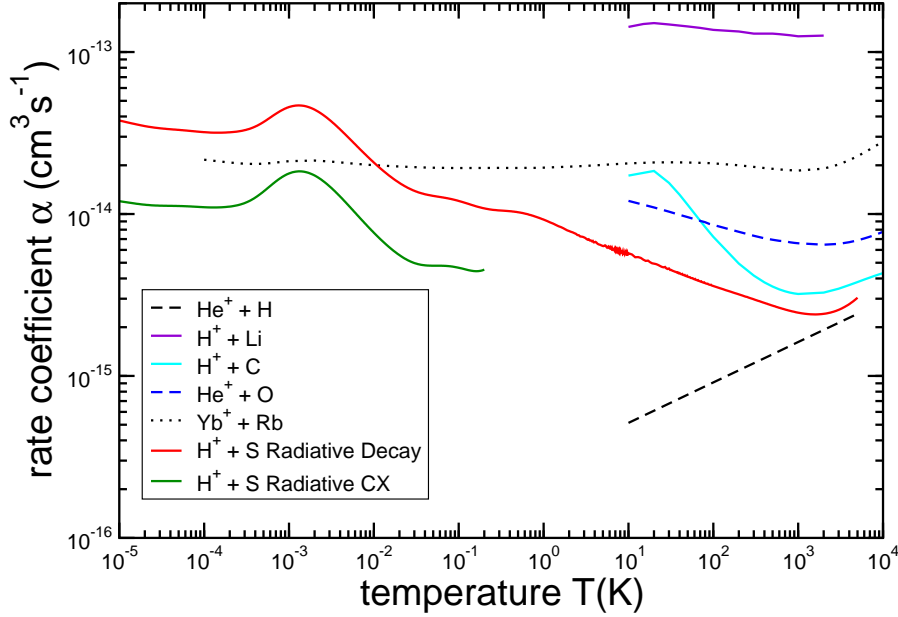


Figure 6. (Colour online) Rate coefficients α (cm^3s^{-1}) as a function of temperature T (K) for the various molecular cations obtained from a Maxwellian average of the radiative charge transfer cross sections, see text for details.

Here the collision problem is solved by directly integrating equation (19) [29, 30, 31]. To distinguish this from the above discussed semiclassical and distorted-wave approximations, we refer to this below as the *quantal approximation*.

As regards the elastic scattering cross section. This is much more problematic. In the ultra cold regime, say sub meV, where one can apply a modified version of effective range theory in which the elastic scattering (real part of the phase shift) can be described by the scattering length. The real phase shift, is extremely difficult to calculate at threshold. The sign and magnitude of the scattering length, connected to the energy of the last bound state below threshold of the well, determines the cross section. Even a small energy shift or correction to the long-range part of the potential, such as hyperfine splitting makes an important contribution, and of course relativistic effects play a role also. However, for the reactive transition described in this paper, the imaginary part of the phase shift, only depends on the short range overlap of the atomic orbitals where the de Broglie wavelength is short, and thus is not sensitive to long-range correlations and corrections. Thus we can be confident in the robustness of our results to such small corrections.

The cross section for total collision-induced radiative decay from the excited state entrance channel, the sum of the cross sections for processes (3) and the process,



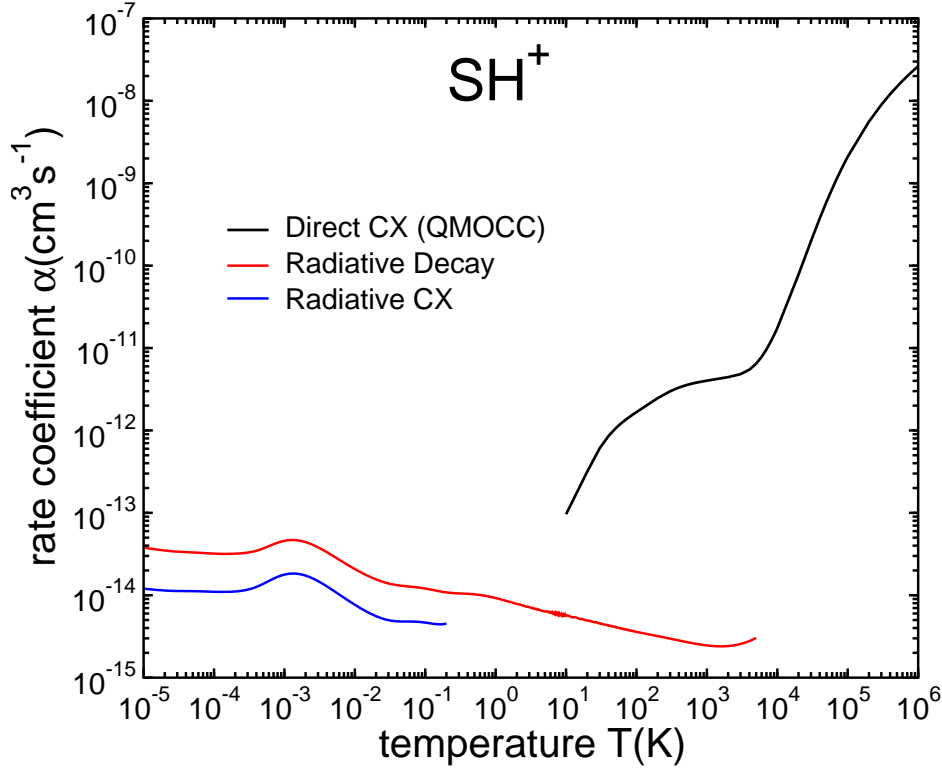


Figure 7. (Colour online) Rate coefficients α (cm^3s^{-1}) as a function of temperature T (K) for $S + H^+$ obtained from a Maxwellian average of the radiative decay cross sections. Results are shown for both the radiative decay (red line), radiative charge transfer (blue line) and a fully Quantal-Molecular-Orbital-Close-Coupling (QMOCC, black line) [5] for direct charge exchange, see text for details.

can be obtained within the optical or quantal approximation. The cross section for collision-induced radiative decay can then be written as,

$$\sigma(E) = \frac{g\pi}{k^2} \sum_{J=0}^{\infty} (2J+1) [1 - e^{-4\mu_J}], \quad (23)$$

where k is given by (16), and g is the statistical weight or approach probability factor, $g = 1/3$ for the $3^3\Sigma^-$ state and $2/3$ for the $3^3\Pi$. At higher energy, a semi-classical approximation may be invoked to calculate the cross sections for radiative decay. The summation over the angular momentum in equation (23) can be replaced by an integral over the impact parameter, b , according to $kb \approx J$. The JWKB approximation can then be used to obtain the elastic scattering wave function,

$$f_J(k, R) \approx \sqrt{\frac{2\mu}{\pi k_{u,J}(R)}} \sin \left(\int_{R_c}^R k_{u,J}(R') dR' + \frac{1}{4}\pi \right). \quad (24)$$

This simplifies the calculation of the phase-shift equation (21) [23, 32, 33] since the rapidly varying integrand gives us (in the classically allowed region) $|f_J(k, R)|^2 \approx$

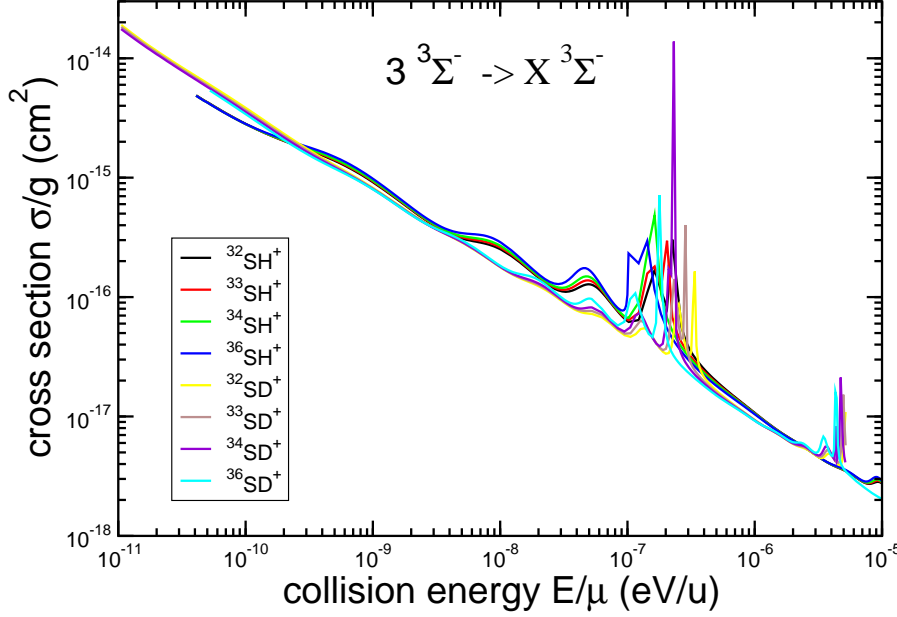


Figure 8. (Colour online) Radiative charge transfer cross section σ (cm^2), for all the various isotopes of Sulfur colliding with H^+ and D^+ ions, as a function of the centre of mass collision energy E (eV) per reduced mass μ , for the dominant $3\ ^3\Sigma^- \rightarrow X\ ^3\Sigma^-$ transition, see text for details.

$\mu/(\pi k_J(R))$. Then using equation (21) we obtain the semi-classical approximation (10).

The velocity averaged rate coefficient $\alpha = \langle v\sigma \rangle$, as a function of temperature T (in Kelvin), is obtained by integrating over the Maxwellian distribution [33]. That is the rate coefficient is given by,

$$\alpha(T) = \left(\frac{8}{\mu \pi k_B^3 T^3} \right)^{1/2} \int_0^\infty E \sigma(E) e^{-E/(k_B T)} dE. \quad (25)$$

We use this expression to evaluate our rates rather than define an effective energy depend rate $v\sigma$ as is normally used in cold collisions [34, 21].

3. Results and Discussion

Cross sections were obtained using the optical potential method with the SH^+ potential energies and transition dipole moments, obtained within the MRCI+Q approximation. Upper limits to the radiative charge transfer cross sections were calculated and are presented in Fig 4. The potentials were shifted to match the experimental asymptotic energies. This shift is quite small as can be seen from Table 1 where comparisons between theory and experiment are presented.

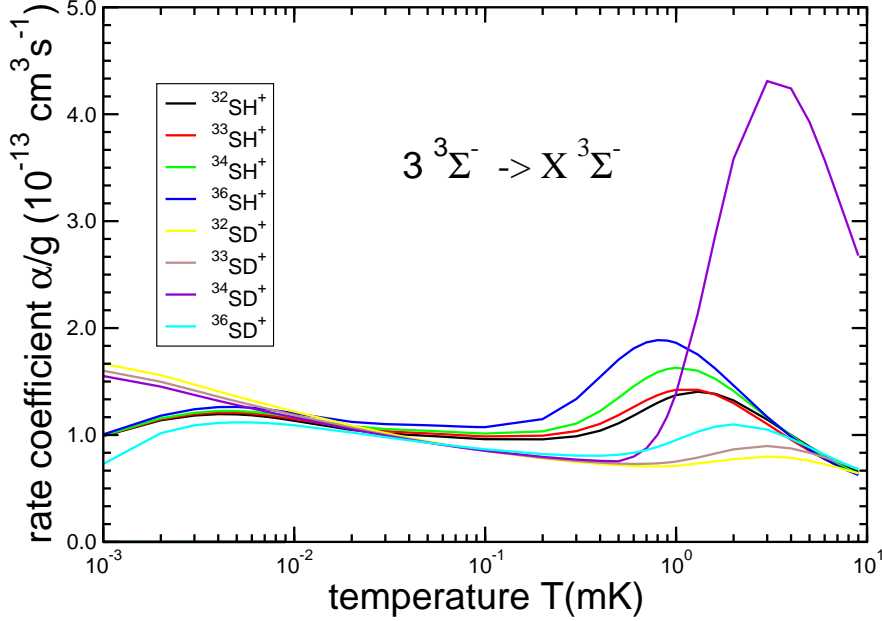


Figure 9. (Colour online) Radiative charge transfer rate coefficient α ($10^{-13} \text{ cm}^3 \text{ s}^{-1}$) for all the various isotopes of Sulfur colliding with H^+ and D^+ ions as a function of the temperature T (mK), for the dominant $3 \text{ } ^3\Sigma^- \rightarrow X \text{ } ^3\Sigma^-$ transition, see text for details.

The dominant transition as can be seen from Figs. 2 and 3 correspond to the $3 \text{ } ^3\Sigma^- \rightarrow X \text{ } ^3\Sigma^-$, while all transitions which originate from the $3 \text{ } ^3\Sigma^-$ electronic state of SH^+ have a Langevin $1/v$ or $E^{-1/2}$ dependence at energies below $\sim 10^{-7}$ eV. Since the $3 \text{ } ^3\Pi$ electronic state is completely repulsive except a small potential barrier at large internuclear distance, transitions which originate with this electronic state are quite small at energies below $\sim 10^{-3}$ eV, but become competitive above ~ 1 eV as they have the largest transition dipole moments (See Fig. 3). Since the $3 \text{ } ^3\Sigma^-$ electronic state of SH^+ is slightly attractive, it can therefore support a number of quasi-bound states which give rise to the large number of resonances superimposed on the background cross sections. The energy dependence of the background cross section follows, to a very good approximation, that derived from the simple semiclassical argument. At the upper limit of the energy range, in the 1-10 eV region we note that the cross section turns upwards for the $3 \text{ } ^3\Sigma^- \rightarrow X \text{ } ^3\Sigma^-$ (black line) and the $3 \text{ } ^3\Sigma^- \rightarrow A \text{ } ^3\Pi$ (blue line), but not for the $3 \text{ } ^3\Sigma^- \rightarrow 2 \text{ } ^3\Pi$ (red line) process. Referring to the energy diagram, Fig. 1 and the moments presented in Figs. 2 and 3, we note that the classical turning point for the entrance channel ($3 \text{ } ^3\Sigma^-$) moves right from 6 a.u. to 4 a.u. over this range. This corresponds to an increasing photon frequency (energy difference) as the kinetic energy of the collision is converted into photon energy, and according to equation 13, an enhanced decay rate. Of course the Franck-Condon factors play an important

part as well. However, while the dipole moment increases for the $3\ ^3\Sigma^- \rightarrow X\ ^3\Sigma^-$ transition, the $3\ ^3\Sigma^- \rightarrow 2\ ^3\Pi$ moment drops sharply as the turning point moves inwards which explains why the cross section for this state continues on a downward slope in this energy region.

Radiative charge transfer has been studied for a variety of other heterogeneous ion-atom systems. The current total cross sections for $H^+ + S$ are compared with cross sections obtained for $He^+ + O$ [20] and $Yb^+ + Rb$ [21] in Fig. 5. Similarly in Fig. 6 we compare the total radiative charge transfer rate coefficients, obtained by averaging over a Maxwellian relative velocity distribution, for these systems and $He^+ + H$ [24], $H^+ + Li$ [35], and $H^+ + C$ [36] collisions. While a clear trend is not evident, the rate coefficients do appear to decrease with neutral atom mass for the case of proton collisions. Furthermore, all rate coefficients have magnitudes between 10^{-16} and $10^{-13}\text{ cm}^3\text{s}^{-1}$, straddling the often adopted canonical value of $10^{-14}\text{ cm}^3\text{s}^{-1}$.

In the ultra cold regime the scattering is dominated by the s-wave and an associated complex scattering length. The sensitivity of the scattering at threshold (zero kinetic energy) to the potential arises from the long de Broglie wavelength and hence the long-range tail of the potential including hyperfine structure which play an important role. Indeed the sign of the real part of the scattering length can vary between hyperfine levels. Our calculations for the inelastic (imaginary part of the phase shift) are localized, due to the dipole moment coupling, and hence not affected by the long-range tail of the potential. Thus we feel confident in our results shown.

Application of the optical potential approach gives the radiative decay cross section which is the sum of radiative charge transfer and radiative association (e.g., equations 3 and 22). We therefore use a fully quantum mechanical two-channel method, described for example in Ref. [35] to compute the radiative charge transfer process directly. As this approach is more computationally demanding, we consider only the dominant transition and a coarser grid of collision energies. As can be seen from Figs. 5 and 6, the radiative charge transfer cross sections and rate coefficients are ~ 3 -5 times smaller than the total radiative decay implying that radiative association (22) dominates for this collision system. As the rate coefficient for the radiative association reaction (1) via $S^+ + H$ for the ground state, is five orders of magnitude smaller than that of reaction (22) for the excited states, the formation of SH^+ may be dominated by $S + H^+$ collisions which should be included in future Sulfur astrochemical models. Explicit radiative association calculations for process (22) will be presented in a future work.

The strength of the radiative decay rate coefficients is governed by the value of the spontaneous Einstein decay rate $\Gamma(R)$ so that the transitions with the largest exothermic potential (asymptotic separated-atom energy differences) typically dominate. Fig. 7 compares the current results for charge transfer due to non-adiabatic transfer for radial and rotational effects [5]. Above 1 K, radiative charge transfer will be unimportant, but it dominates charge transfer in the cold and ultra-cold regimes for this system.

Finally, in Figs. 8 and 9, we illustrate the isotope effect on radiative decay of the dominant transition for all isotopes of Sulfur colliding with H^+ and D^+ . Plotting the cross sections as functions of the centre of mass kinetic energy divided by the reduced mass, we find that the cross section is insensitive to the reduced mass, at least for the considered energy range and in regions away from the resonances. The rate coefficients, shown in Fig. 9, are nearly temperature independent, as expected, but also reduced mass independent except for the broad resonance feature between

$\sim 3 \times 10^{-4}$ and $\sim 8 \times 10^{-3}$ K. The strength of this resonance increases with reduced mass within each H^+ or D^+ sequence, except for the case of $^{34}SD^+$, which has a rate coefficient near 3 mK ~ 4 times larger than all other isotopes.

4. Conclusions

Radiative charge transfer for collisions of S atoms with protons has been studied within the optical potential method for nine electronic transitions and a large range of cold and ultracold kinetic energies. A fully quantal approach including radiative charge transfer is also applied. The lower limit for the total rate coefficients are found to be $\sim 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ and virtually independent of temperature. This value is smaller than for most other collision systems except for $He^+ + H$ [24]. Above ~ 1 K, non-adiabatic effects in charge transfer for $H^+ + S$ collisions need to be incorporated.

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